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The Influence of the Equilibrium Dissociation of a Diatomic Gas on Brayton-Cycle Performance

16 JANUARY 1962

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and
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Prepared for DEPUTY COMMANDER AEROSPACE SYSTEMS
AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE
Inglewood, California

LABORATORIES DIVISION • AEROSPACE CORPORATION
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THE INFLUENCE OF THE EQUILIBRIUM DISSOCIATION OF A DIATOMIC GAS ON BRAYTON-CYCLE PERFORMANCE

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PREFACE

Drs. T. A. Jacobs and J. R. Lloyd collaborated on a portion of the research reported in this document while affiliated with the California Institute of Technology, Pasadena, California.

ABSTRACT

By employing the Lighthill "ideal dissociating gas" approximation, the influence of the equilibrium dissociation of a diatomic molecule on Brayton-cycle performance is demonstrated. For low temperature ratios it is shown that the use of a suitably selected molecule results in a significant improvement in cycle thermal efficiency.

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INTRODUCTION

In an earlier paper we investigated the influence of molecular vibration on Brayton-cycle performance by employing the harmonic oscillator approximation [1].[1] This approximation allowed us to write the equations describing the cycle performance in a convenient dimensionless form, thus admitting a considerable degree of generality in our analysis. In this paper we treat the influence of equilibrium gas dissociation on Brayton-cycle performance. A convenient dimensionless form is achieved by employing the approximations introduced by Lighthill [2]. An objection which could possibly be raised in our use of the Lighthill approximation in this application is that it embodies the assumption that the contribution of molecular vibration to the specific heat is frozen at one-half of the classical value for complete excitation. In our earlier work, however, we have demonstrated the influence of molecular vibration on cycle performance to be insignificant.

In the succeeding sections we show that gas dissociation implies the existence of at least one extremum in the cycle thermal efficiency.[2] We then present the thermodynamic analysis and discuss the influence of gas dissociation on Brayton-cycle performance.

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[1] Numbers in brackets designate References at end of paper.

[2] This extremum should not be confused with the maximum implied by the introduction of component efficiencies, i.e., turbine and compressor efficiencies.

EXISTENCE OF EXTREMA

Following our earlier argument [1] it may be shown that the maximum thermal efficiency, η^{o}_{TH}, of a Brayton-cycle for which the specific heat is a constant is given by an expression which is independent of the specific heat and is of the form

$$\eta^{o}_{TH} = f\left(\eta_c, \eta_t, \frac{T_3}{T_1}\right) \tag{1}$$

Here, η_c and η_t are the efficiencies of the compressor and turbine, respectively; T is the absolute temperature; and the subscripts refer to points on the cycle as shown in Fig. 1. Now, for a dissociating diatomic gas at sufficiently low temperature, the degree of dissociation is negligible and, hence, the specific heat is constant if we neglect the contribution of the vibrational mode of motion. At sufficiently high temperatures the gas is completely dissociated and, again, the specific heat is constant. At these extremes the maximum thermal efficiency is given by Eq. (1). It then follows that at least one extremum exists for intermediate degrees of dissociation. One is thus moved to investigate by detail analysis the nature of the extrema with a view toward possible improvement in cycle performance.

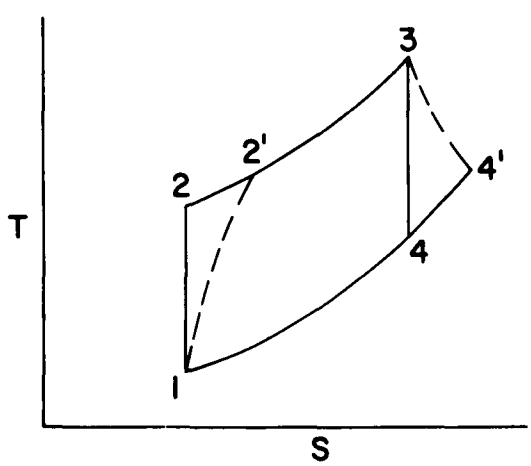

Fig. 1. Temperature-Entropy (S) Diagram for the Brayton-Cycle

THERMODYNAMIC ANALYSIS

Consider a diatomic species, A_2, that dissociates according to the equation

$$A_2 \rightleftarrows 2A \quad . \tag{2}$$

If α represents the fraction of A_2 dissociated, then the Lighthill "ideal dissociating gas" approximation [2] gives

$$\frac{\alpha^2}{1 - \alpha} = \frac{\rho_d}{\rho} e^{-D/RT} \quad . \tag{3}$$

Here,

ρ_d = a constant for a particular gas,[3]

ρ = the actual gas density,

D = the dissociation energy per mole of the particular molecule at $0^{\circ}K$,

R = the universal gas constant, and

T = the absolute temperature.

It is now convenient to introduce T_d, ρ_d, P_d and U_d as units, of temperature, density, pressure, and specific internal energy, respectively, where T_d, P_d, and U_d are defined by the relations

$$T_d \equiv \frac{D}{R} \quad , \tag{4}$$

$$P_d \equiv \frac{R}{W} \rho_d T_d \quad , \tag{5}$$

$$U_d \equiv \frac{D}{W} \quad , \tag{6}$$

[3] A method for rapid calculation of ρ_d is given in the appendix.

and where W is the molecular weight of A_2. In these units, Eq. (3) becomes

$$\frac{\alpha^2}{1-\alpha} = \frac{1}{\rho} e^{-1/T} \quad , \tag{7}$$

and the perfect gas law and specific enthalpy (also in units of U_d) may be written, respectively, as

$$P = \rho T(1+\alpha) \tag{8}$$

and

$$h = u + \frac{P}{\rho} = (4+\alpha)T + \alpha^4 \quad . \tag{9}$$

Along reversible isentropic paths we may also write

$$dS = \frac{dh}{T} - \frac{dP}{T} = 0 \quad . \tag{10}$$

Equations (8), (9), and (10) may be combined to give the following differential equation relating the temperature and pressure along isentropic paths:

$$\frac{P}{T}\frac{dT}{dP} = \frac{1+\alpha+\frac{1}{2}\left(1+\frac{1}{T}\right)\frac{P}{T}\left(\frac{\alpha^3}{e^{-1/T}}\right)}{4+\alpha+\frac{1}{2}\alpha(1-\alpha^2)\left(1+\frac{1}{T}\right)^2} \quad . \tag{11}$$

With the equations above we can now determine the maximum thermal efficiency of a simple Brayton-cycle including the influence of gas dissociation. Referring to Fig. 1, the thermal efficiency, η_{TH}, is given by

---

[4] Implicit in this statement of the enthalpy is the approximation that the vibrational motion is frozen at one-half the maximum classical value of RT.

$$\eta_{TH} = 1 - \frac{h_{4'} - h_1}{h_3 - h_{2'}} \tag{12}$$

The component efficiencies are defined as

$$\eta_c \equiv \frac{h_2 - h_1}{h_{2'} - h_1} \tag{13}$$

and

$$\eta_t \equiv \frac{h_3 - h_{4'}}{h_3 - h_4} \tag{14}$$

For a given initial pressure, P_1, and specified values of T_3/T_1, η_c and η_t, Eqs. (7) through (9) and (11) through (14) allow us to determine η_{TH} for any assumed value of T_2/T_1. By systematic variation of T_2/T_1, the value of T_2/T_1 which maximizes the thermal efficiency may be found. We denote this maximum of the thermal efficiency by η^*_{TH}. The actual calculations are best carried out numerically, and we have programmed these equations for the IBM 709 digital computer. The nature of the solutions obtained is indicated in Figs. 2, 3, and 4, where for all cases we have taken η_c and η_t to be 0.85.

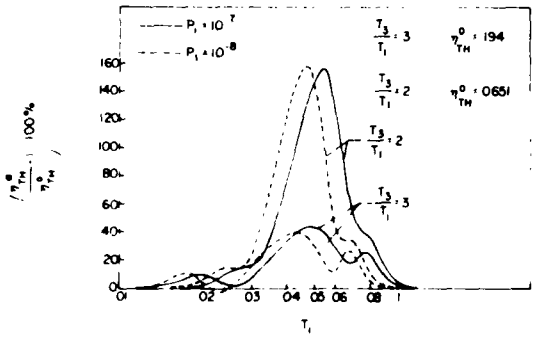

Fig. 2. Variation of Optimum Thermal Efficiency with Characteristic Dissociation Parameter, $T_1 = RT_{sink}/D$

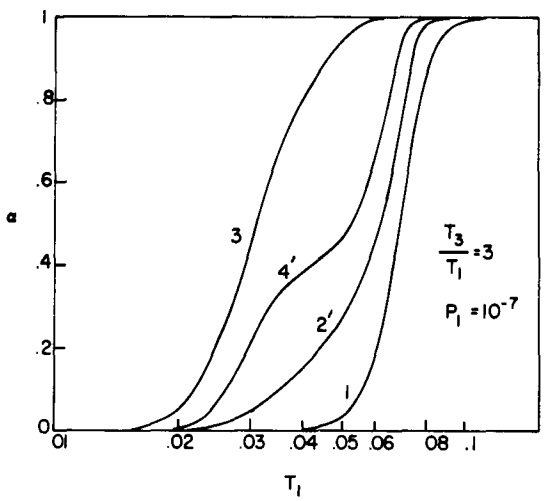

Fig. 3. Variation of the Fraction of Gas Dissociated with Characteristic Dissociation Parameter, $T_1 = RT_{sink}/D$

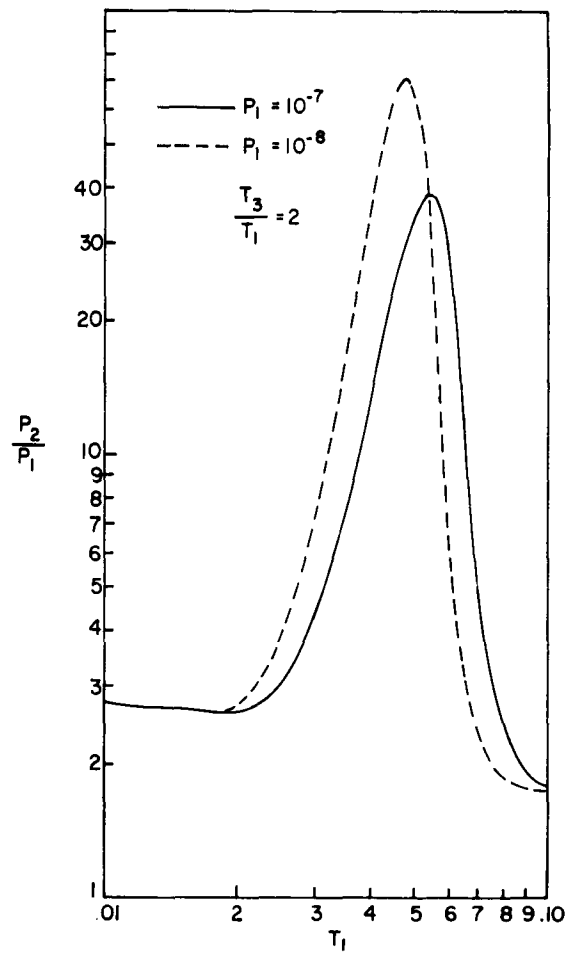

Fig. 4. Variation of Pressure Ratio with Characteristic Dissociation Parameter

DISCUSSION

In Fig. 2 we show the influence of gas dissociation in cycle performance in terms of the percentage change in maximum thermal efficiency as compared to the maximum thermal efficiency for a cycle in which the specific heat is constant. It will be recalled that temperature was made dimensionless with respect to the bond dissociation energy and, thus, one may "move" along the abscissa in our figures either by changing the dissociation energy or the sink temperature. We shall call T_1 the characteristic dissociation parameter. It may be seen from the figure that a considerable improvement in cycle efficiency can be achieved by a judicious selection of diatomic molecules.

The influence of dissociation is seen to be greatest for low temperature ratios; however, low temperature ratios are not devoid of practical application, since it may be readily shown that temperature ratios of less than two are required by those space power plants which are radiator weight limited.

It is interesting to note that a number of maxima and minima are exhibited by our solution. The reason for these extrema may be inferred from Fig. 3, in which we display for one of the cases shown in Fig. 2 the fraction of gas dissociated at various points in the cycle. The numbers on the curves refer to the corresponding points on the cycle, Fig. 1. As an example, the first maximum in Fig. 2 may be explained by noting that the gas is entering the turbine (point 3) partially dissociated. For a small range on the abscissa the gas leaves the turbine completely associated, the energy of association appearing as turbine work so that the cycle efficiency increases. Continuing along the abscissa, however, dissociated gas begins to appear at the turbine exit (point 4). The remaining energy of association carried by the gas is lost during the heat rejection part of the cycle, and the efficiency begins to fall.

In Fig. 4 is shown the pressure ratios required to achieve the efficiencies shown above. These rather large pressure ratios could present a severe restriction for practical application.

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At a number of meetings concerning space power plants that the authors have attended in the past, a frequent suggestion for improving performance has been the use of equilibrium dissociating gases. Indeed, Prof. Lighthill makes this suggestion in his paper. To our knowledge, no calculations have been forthcoming. In this paper we have clearly indicated, for diatomic molecules, the magnitude of improvement that can be expected, and it appears to be appreciable. Further study with a view toward application is suggested.

APPENDIX

In this appendix we show a rapid method for the calculation of the parameter ρ_D introduced by Lighthill [2].

For the chemical reaction given by Eq. (2), the equilibrium constant, Kp, is defined as

$$Kp = \frac{P_A^2}{P_{A_2}} \quad . \tag{15}$$

Here, P_A and P_{A_2} are the partial pressures of atom A and molecule A_2, respectively. In terms of α, the mole fraction of A is $2\alpha/(1 + \alpha)$, and of A_2 is $(1 - \alpha)/(1 + \alpha)$. Hence, Eq. (15) may be written

$$Kp = \frac{4\alpha^2}{1 - \alpha^2} P \quad , \tag{16}$$

where P is the total gas pressure.

From the fundamental thermodynamic formula [3],

$$Kp = e^{-\Delta F^o/RT} \quad , \tag{17}$$

ΔF^o being the change in free energy produced by the reactants when they are in their defined standard states.

We may write, of course, the tautology

$$Kp = e^{-1/R\ \Delta[(F^o - D)/T]}\ e^{-D/RT} \tag{18}$$

where D is the bond dissociation energy, as before. Equations (16) and (18) along with the perfect gas formula then combine to yield

$$\frac{a^2}{1-a} = \left\{\frac{W}{4RT}\, e^{-1/R\,\Delta[(F^o - D)/T]}\right\} \frac{1}{\rho}\, e^{-D/RT} \quad . \tag{19}$$

Apparently, the quantity in brackets is to be identified with ρ_D, i.e.,

$$\rho_d = \frac{W}{4RT}\, e^{-1/R\,\Delta[(F^o - D)/T]} \quad . \tag{20}$$

The value of $\Delta[(F^o - D)/T]$ has been tabulated as a function of temperature for a large number of substances [4]. As Lighthill has pointed out, ρ_d shows a very weak temperature dependence for many diatomics.

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